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Article

Preparation of N-vacancy-doped g-C₃N₄ with outstanding photocatalytic H₂O₂ production ability by dielectric barrier discharge plasma treatment

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ABSTRACT

Dielectric barrier discharge (DBD) plasma is considered to be a promising method to synthesize solid catalysts. In this work, DBD plasma was used to synthesize a nitrogen-vacancy-doped g-C₃N₄ catalyst in situ for the first time. X-ray diffraction, N₂ adsorption, ultraviolet-visible spectroscopy, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy, electron paramagnetic resonance, O₂ temperature-programmed desorption, and photoluminescence were used to characterize the obtained catalysts. The photocatalytic H₂O₂ production ability of the as-prepared catalyst was investigated. The results show that plasma treatment influences the morphology, structure, and optical properties of the as-prepared catalyst. Nitrogen vacancies are active centers, which can adsorb reactant oxygen molecules, trap photoelectrons, and promote the transfer of photoelectrons from the catalyst to the adsorbed oxygen molecules for the subsequent reduction reaction. This work provides a new strategy for synthesizing g-C₃N₄-based catalysts.

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1. Introduction

Since Fujishima et al. [1] discovered photocatalytic phenomena in the photodecomposition of water on *n*-type TiO₂ semiconductor electrodes, heterogeneous photocatalysis has attracted the attention of many scholars in the fields of chemistry, physics, materials science, and environmental protection. An increasing number of semiconductor materials have been found to be suitable for photocatalytic reactions [2–6]. Generally, there are three main factors that determine photocatalytic performance [7]. First, during photoexcitation, the light absorption ability of a catalyst defines how many electron-hole pairs can be produced. Secondly, during the migration of electron-hole pairs, the separation rate determines how many

electron-hole pairs contribute to the photocatalytic reaction. Lastly, during the photocatalytic reaction, the surface area defines how many reactants can react at the same time.

In 2009, Wang et al. [8] observed that graphitic carbon nitride (g-C₃N₄) has excellent performance in the photocatalytic decomposition of water to produce hydrogen, thus initiating an upsurge in the research of g-C₃N₄-based photocatalytic materials. Owing to its advantages of a suitable band gap, high chemical stability, and unique electronic structure, g-C₃N₄ has shown excellent potential for application in photocatalytic hydrogen production, organic pollutant degradation, organic synthesis, nitrogen fixation, and hydrogen peroxide production [9–20]. Preparation methods of g-C₃N₄ reported in the literature mainly include solvothermal synthesis [21], solid-state synthesis

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[22,23], electrochemical deposition [24], and thermal polymerization [25,26]. However, these methods have the disadvantages of being environment-unfriendly and time-consuming, as well as having harsh reaction conditions, low efficiency, and high energy consumption. Therefore, finding an environment-friendly and energy-efficient preparation method is an urgent issue that must be addressed.

Plasma—a special state different from the conventional gas, liquid, and solid states—is known as the fourth state of matter. It is a quasi-electrically neutral aggregate composed of a large number of electrons, ions, atoms, molecules, free radicals, and other particles. There are many ways to generate plasma, including high temperatures, electric discharges, and high-energy particle beams. The use of high-voltage discharges is the most commonly used method to obtain plasma in the laboratory and for industrial applications. Based on its power characteristics, a discharge can be classified as a direct-current discharge, radio-frequency discharge, microwave discharge, or dielectric barrier discharge (DBD). The DBD method is advantageous because it does not require vacuum conditions, it can be performed under atmospheric pressure, it easily achieves a large discharge area, and it achieves relatively stable discharges. Additionally, the temperature of neutral particles and ions during DBD is much lower than the electron temperature; thus, a large number of active species can be generated by inelastic electron collisions, triggering a series of physicochemical changes that are difficult to obtain by conventional methods. Based on the above advantages, the DBD method is widely used in the theoretical research of laboratories, such as in material synthesis [27], volatile-organic-compound treatment [28,29], automotive exhaust-gas purification [30,31], and material-surface treatment [32]. Moreover, researchers have investigated the modification of catalysts using DBD plasma. Treating a catalyst in a plasma atmosphere of different gases can significantly affect the properties of the catalyst, such as by changing the acidic strength of catalyst, increasing its hydrophilicity, affecting its electronic structure, promoting the dispersion of its active component, or creating a new active phase [33–36].

Reports on the synthesis and modification of photocatalysts using DBD plasma are rare and mainly focus on TiO₂-based photocatalysts [37–40]. Luo et al. [37] prepared Cu₂O/N-TiO₂ catalysts using DBD plasma in a mixed N₂-Ar atmosphere. The photodegradation of methyl orange over the as-prepared catalyst was markedly promoted under both visible and full-spectrum light compared with pure TiO₂ and Cu₂O/TiO₂. El-Roz et al. [38] prepared a TiO₂-beta zeolite composite catalyst using DBD plasma in an O₂ atmosphere. The composite catalyst prepared by plasma treatment exhibited 8 times higher methanol photodegradation rates than that of a P25 catalyst (commercial TiO₂). Hu et al. [39] prepared a Ni/NiO/N-TiO_{2-x} heterojunction catalyst using DBD plasma in an NH₃ atmosphere. The hydrogen production rate of the prepared catalyst was up to 1210 mmol·h⁻¹, which is 250 times higher than that of pure TiO₂, and its apparent quantum yield was 7.5%. Hu et al. [40] also used DBD plasma to modify TiO₂ in a mixed H₂-CCl₄ atmosphere. The results showed that the Cl radical generated by the modification is favorable for the photodegradation of aromatic-ring

gas pollutants. To date, the preparation of g-C₃N₄ using DBD plasma has not been reported in the literature.

H₂O₂, as a green oxidant, has important applications in many fields, such as organic synthesis, water treatment, and catalysis. The anthraquinone process is widely used in the industry to produce hydrogen peroxide. This method consumes an enormous amount of energy and is unsuitable for the current concept of using “green, energy saving and environmentally friendly” techniques in the chemical industry. In recent years, photocatalytic hydrogen-peroxide production technology has attracted great interest from researchers [41,42]. Oxygen reacts with hydrogen ions in water via a two-electron reduction reaction to generate hydrogen peroxide. The reaction is as follows: O₂ + 2H⁺ + 2e⁻ → H₂O₂. In this work, g-C₃N₄ doped with N vacancies was prepared for the first time by DBD plasma treatment under H₂ atmosphere. The effects of the N vacancies on the structural and optical properties and the H₂O₂ production ability of catalysts are examined in detail.

2. Experimental

2.1. Preparation

The g-C₃N₄ was synthesized in a DBD reactor, which was used in our previous work [39,40]. In each run, 0.5 g of melamine was placed in a quartz tube. Ar was allowed to pass through the quartz tube for 5 min to flush out the air. A high voltage of ~10 kV was supplied by a plasma generator under a constant H₂ flow (40 mL·min⁻¹). The power input was 50 V × 0.4 A, the discharge frequency was 10 kHz, and the discharge was maintained for 15–45 min. Subsequently, the reactor was cooled to room temperature. In the following, the obtained g-C₃N₄ is denoted as PLCN-*x*, where *x* stands for the discharge time (min). For comparison, melamine was annealed at 520 °C for 2 h at a rate of 5 °C·min⁻¹; the obtained catalyst is denoted as gCN.

2.2. Characterization

The X-ray diffraction (XRD) patterns of the samples were recorded using a Rigaku D/max-2400 instrument and Cu-K_α radiation (λ = 1.54 Å). Ultraviolet-visible (UV-Vis) spectroscopy was performed using a UV-Vis spectrophotometer (JASCO V-550) and BaSO₄ as the reflectance sample. The morphologies of the samples were observed by scanning electron microscopy (SEM; JSM 5600LV, JEOL Ltd.). Transmission electron microscopy (TEM) images were obtained with a Philips Tecnai G220 microscope. X-ray photoelectron spectroscopy (XPS) measurements were performed using a Thermo Escalab 250 XPS system with Al-K_α radiation as the excitation source. Nitrogen adsorption-desorption was measured at -196 °C with a Micromeritics 2010 analyzer. The BET surface area (*S*_{BET}) was calculated based on the adsorption isotherm. Elemental analysis was performed using a Vario EL cube from Elementar Analysensysteme GmbH. Temperature-programmed desorption (TPD) studies were conducted using a CHEMBET-3000 (Quantachrome, USA) instrument. Photoluminescence (PL)

spectra were measured with a fluorospectrophotometer (FP-6300) using a Xe lamp as the excitation source. Electrochemical impedance spectra (EIS) were acquired with an EIS spectrometer (EC-Lab SP-150, BioLogic Science) in a three-electrode cell.

2.3. Photocatalytic reaction

The catalyst (0.2 g) was added into 200 mL of deionized water while stirring to form a suspension. Ethanol with a concentration of $0.789 \text{ g}\cdot\text{L}^{-1}$ was included as a hole scavenger. Then, the suspension was exposed to a 250-W high-pressure sodium lamp with main emission from 400 to 800 nm. The UV light portion of the sodium lamp was filtered by a NaNO_2 solution ($0.5 \text{ mol}\cdot\text{L}^{-1}$). O_2 was bubbled ($80 \text{ mL}\cdot\text{min}^{-1}$) during the photoreaction process. All experiments were conducted at ambient pressure and 30°C . At given time intervals, 5-mL aliquots of the suspension were collected and immediately centrifuged to obtain liquid samples. The H_2O_2 concentration was analyzed by the standard iodometric method [43,44].

3. Results and discussion

3.1. Characterization

The XRD patterns of the prepared catalysts are shown in Fig. 1. gCN has two characteristic peaks, located at $2\theta = 13.1^\circ$ and 27.5° , respectively. Between them, the diffraction peak at 27.5° is the characteristic peak of the interlayer stacking of the aromatic segments, which has a Miller index of (002). The diffraction peak at 13.1° is assigned to the melon-like structure, which has a Miller index of (100). These two characteristic peaks are in agreement with those reported in the literature [8]. Compared with gCN, PLCN-15 has obvious impurity peaks at $2\theta = 18^\circ$ and 26° , indicating that the condensation was incomplete. This may be due to the short period of plasma treatment. In contrast, the two catalysts obtained by plasma treatment for more than 30 min show a complete crystal structure of $\text{g}\cdot\text{C}_3\text{N}_4$, indicating that $\text{g}\cdot\text{C}_3\text{N}_4$ can be successfully prepared by plasma treatment for more than 30 min. Additionally, the characteristic peaks of PLCN-15 and PLCN-30 at 27.5° are significantly weak-

Fig. 1. XRD patterns of gCN and plasma treated catalysts.

Fig. 2. SEM images of as-prepared gCN (a), PLCN-15 (b), PLCN-30 (c), and PLCN-45 (d).

er than those of gCN, while the intensity of PLCN-45 is similar to that of gCN. The results suggest that a short plasma treatment time results in the formation of $\text{g}\cdot\text{C}_3\text{N}_4$ with a small particle size, and the particle size of the catalyst increases as the plasma treatment time is extended. The amplification of the 25° – 30° region shows that the characteristic peak position of the catalyst prepared by plasma treatment is obviously shifted compared with that of gCN, which may be due to the lattice defects of the $\text{g}\cdot\text{C}_3\text{N}_4$.

Fig. 2 displays the SEM results of the catalysts. It is clear that all the prepared catalysts show a plate-like structure with no regular morphology. The particle sizes of PLCN-15 and PLCN-30 are obviously smaller than that of PLCN-45, which is comparable to gCN. This is consistent with the XRD results. TEM and high-resolution TEM (HRTEM) images of PLCN-30 are presented in Fig. 3. As shown in Fig. 3(a), PLCN-30 shows a layer structure with no pores after the plasma treatment. A typical HRTEM image of PLCN-30 exhibits a clear lattice fringe (Fig. 3(b)). The measured lattice spacing is 0.330 nm, very close to the (0 0 2) crystal face of graphitic carbon nitride [45]. This confirms that graphitic carbon nitride was successfully synthesized by the plasma treatment.

The N_2 adsorption-desorption isotherms for the prepared catalysts are shown in Fig. 4. All catalysts exhibit type-IV isotherms. BET of gCN is as small as $9.2 \text{ m}^2\cdot\text{g}^{-1}$, whereas these of PLCN-15 and PLCN-30 are as high as 20.5 and $21.2 \text{ m}^2\cdot\text{g}^{-1}$, respectively, much higher than that of gCN. Combined with the

Fig. 3. TEM (a) and HRTEM (b) images of PLCN-30.

Fig. 4. N_2 adsorption-desorption isotherms of gCN and plasma treated catalysts.

Fig. 5. UV-Vis spectra of gCN and plasma treated catalysts.

SEM results, these findings suggest that the increased surface areas may be due to the smaller particle size of the catalyst prepared by the plasma process. These g- C_3N_4 nanoparticles aggregate to form many secondary pores, resulting in a significant increase in specific surface area. This increase can expose more reactive centers and enable more reactants to react simultaneously, which has a crucial effect on catalyst performance. The specific surface area of PLCN-45 is significantly reduced to $9.7 \text{ m}^2 \cdot \text{g}^{-1}$, which may be due to the prolonged plasma treatment time.

Fig. 5 displays the UV-Vis spectra of the prepared catalysts. All catalysts show the typical absorption spectra of graphitic carbon nitride semiconductor with an absorption boundary at approximately 465 nm. Plasma treatment slightly shifts this boundary and enhances the absorption of visible light. The band gaps of gCN, PLCN-15, PLCN-30, and PLCN-45 were calculated according to the formula to be 2.67, 2.63, 2.59, and 2.55 eV, respectively [46]. It is worth noting that, unlike gCN, the catalysts prepared by the plasma method exhibited a certain degree of visible light absorption with wavelengths longer than 500 nm. According to the literature, this may be due to the presence of lattice defects in the g- C_3N_4 catalyst [47,48]. This finding is consistent with the XRD results. For verification, we performed elemental analysis of the catalyst. The results show that the C/N ratio of gCN is 0.74, which is similar to the theoretical C/N ratio of g- C_3N_4 . The C/N ratios of PLCN-15, PLCN-30, and PLCN-45 are 0.78, 0.81, and 0.82, respectively,

much higher than that of gCN. Thus, we deduce that the lattice defects in g- C_3N_4 are nitrogen vacancies, and longer plasma treatment times result in a higher content of nitrogen vacancies.

To confirm the position of the N vacancies, XPS spectra were obtained, as shown in Fig. 6. In the N 1s region (Fig. 6(a)), the two contributions of gCN located at 398.5 and 400.2 eV are assigned to sp^2 -hybridized aromatic nitrogen atoms bonded with carbon atoms (C–N=C) and nitrogen atoms bonded with three carbon atoms (N– C_3). For PLCN-30, no obvious difference in the peak position is observed. However, the peak area ratio of [N– C_3]/[C–N=C] decreases from 0.27 for gCN to 0.25 for PLCN-30, clearly indicating that nitrogen vacancies are primarily located at the tertiary nitrogen lattice sites. For the C 1s region (Fig. 6(b)), the three contributions located at 284.6, 286, and 288.4 eV for both samples are attributed to: (1) C–C bonds originating from sp^2 C atoms bonded with N in an aromatic ring (N–C=N); (2) C=N or C $\equiv$ N bonds, which could be attributed to defect-containing sp^2 -hybridized carbon atoms present in graphitic domains; and (3) pure graphitic sites in a CN matrix. Note that in addition to the three C 1s peaks mentioned above, a new peak at a high binding energy of 290 eV appears in PLCN-30. This peak is attributed to the two-coordinated carbon (N–C–N) formed by the disappearance of three-coordinated nitrogen, thereby confirming the generation of nitrogen vacancies. In conclusion, nitrogen vacancies are primarily located at the tertiary nitrogen lattice sites. The VB XPS spectra of gCN and

Fig. 6. XPS spectra of PLCN-30 and gCN in the region of N 1s (a), C 1s (b) and VB XPS (c).

PLCN-30 are shown in Fig. 6(c). The VB maxima of gCN and PLCN-30 are shown to be +1.52 and +1.24 V, respectively. This indicates that the nitrogen vacancies cause an obvious shift of the band position. Combined with the band-gap energies obtained from the UV-Vis spectra, the CB positions of gCN and PLCN-30 are calculated to be −1.15 and −1.35 V, respectively.

Fig. 7 shows the EIS results of the prepared catalysts. The plot shows that the semicircle radius of gCN is the largest, which indicates that the charge-transfer resistance is large and unfavorable to charge transport [49]. The semicircle radius of the catalyst prepared by the plasma method decreases significantly, indicating that nitrogen vacancies are conducive because they reduce the resistance of the catalyst's solid-interface layer and improve the electron-transfer efficiency. The semicircle radius of the catalyst prepared by the plasma method increases in the order PLCN-30 < PLCN-45 < PLCN-15, that is, the electron-transfer efficiency of the catalyst first increases and then decreases with the extension of the plasma treatment time. In the initial stage, with prolonged plasma treatment time, the crystal structure of carbon nitride forms gradually, and the electron-transfer efficiency increases. When the duration of the plasma treatment is longer than 30 min, the agglomeration of carbon nitride leads to increased particle size and decreased specific surface area. As a result, the migration distance of electrons from the bulk phase to the surface increases, which induces a decrease in the migration efficiency.

The photogenerated-carrier separation efficiency has a significant effect on the catalyst performance, and the effective separation of photogenerated electron-hole pairs can ensure the presence of sufficient photoelectrons to reduce the number of oxygen molecules forming H_2O_2 . Fig. 8(a) shows the PL spectra of the catalysts under oxygen atmosphere. Generally, lower PL peak intensity indicates higher electron-hole pair separation efficiency. Strong fluorescence emission peaks were detected for all four catalysts at 460–470 nm, which is in good agreement with the absorption boundary in the UV-Vis spectra. Fluorescence quenching was observed in the spectra of the catalysts prepared by the plasma method, indicating that nitrogen vacancies can trap photoelectrons and increase the electron-hole separation efficiency of the catalyst, which is consistent with the EIS result. Fig. 8(b) shows a comparison of the PL spectral intensities of gCN and PLCN-30 under Ar and

oxygen atmospheres, respectively. The figure demonstrates that the PL spectra of gCN are basically the same in both atmospheres, which indicates that the atmosphere has no effect on the gCN electron-hole separation efficiency. Interestingly, the PL intensity of PLCN-30 under oxygen atmosphere is much lower than that under Ar atmosphere. This may be attributed to the oxygen atmosphere playing a part in the electron transfer of the catalyst; that is, the nitrogen vacancies on the surface of PLCN-30 can trap photoelectrons and promote the transfer of photoelectrons from the catalyst to the adsorbed oxygen molecules, thus reducing the recombination rate.

EPR provides direct evidence of defects, such as oxygen and nitrogen vacancies, on the surface of the catalyst [47,50]. As shown in Fig. 9(a), no signal peak exists in the EPR spectrum of gCN, which indicates that gCN does not have a single unpaired electron. However, the PLCN-30 contains a clear signal peak at $g = 2.003$, indicating the existence of a single unpaired electron in the catalyst, which is due to the presence of nitrogen vacancies in PLCN-30 [47,50]. O_2 TPD was used to investigate the oxygen absorption ability of the catalyst, and the results are shown in Fig. 9(b). Almost no O_2 -TPD signal is observed for gCN, indicating that gCN has low oxygen absorption ability. However, the catalyst prepared by the plasma method has a strong desorption peak signal in the range 350–600 °C, indicating that nitrogen vacancies can significantly improve the oxygen absorption ability of the catalyst. The desorption peak signal first increases and then decreases with increasing plasma treatment time. In the initial stage, the content of nitrogen

Fig. 7. EIS of gCN and plasma treated catalysts.

Fig. 8. PL spectra of as-prepared catalysts under O_2 atmospheres (a) and the comparison of PL intensity of gCN and PLCN-30 under Ar and O_2 atmospheres (b).

Fig. 9. EPR spectra (a) and O₂-TPD (b) profiles of as-prepared catalysts (b).

vacancies on the surface of the catalyst increases with increasing plasma treatment time, which improves the oxygen adsorption ability. When the plasma treatment time is longer than 30 min, although the content of the nitrogen vacancies increases further, a large number of nitrogen vacancies are not exposed on the surface owing to the reduction of the specific surface area. Thus, oxygen molecules cannot be adsorbed, resulting in an inverse decrease of the O₂-TPD signal peak. Based on the above characterization results, we conclude that the nitrogen vacancies are active centers, which can adsorb reactant oxygen molecules and trap photoelectrons, thus promoting the transfer of photoelectrons from the catalyst to the adsorbed oxygen molecules for the subsequent reduction reaction.

3.2. Photocatalytic performance

Fig. 10(a) displays the H₂O₂ production ability of the as-prepared catalysts. Obviously, the H₂O₂ concentration increases with increasing reaction time. When the reaction time reaches 12 h, the H₂O₂ concentration reaches the maximum and exhibits almost no further change. This level corresponds to the steady state, where the rate of H₂O₂ production is equal to its rate of consumption [51,52]. The H₂O₂ formation and decomposition rates follow zero- and first-order kinetics, which can be described by the following equation [H₂O₂] =

$(k_f/k_d)[1 - \exp(-k_d t)]$. In this equation, k_f and k_d denote the rate constants of H₂O₂ formation and decomposition, respectively [53–54]. The calculated results are listed in Table 1, which shows that gCN exhibits the lowest H₂O₂ concentration, k_f , and k_d . PLCN-15 has a H₂O₂ concentration of 1.0 mmol·L⁻¹, only 2.5 times higher than that of gCN. This is probably due to the incomplete g-C₃N₄ structure, caused by the short plasma treatment time. PLCN-30 exhibits the highest H₂O₂ concentration, 4.4 mmol·L⁻¹, which is 11 times higher than that of gCN. This is because its increased surface area results in more N vacancies exposed to the surface, allowing more oxygen to be reduced at the same time, thus leading to increased formation rate. In the case of PLCN-45, the H₂O₂ concentration decreases to 3.0 mmol·L⁻¹, and the k_f and k_d values also decrease. This could be due to the reduced number of active sites owing to the drastically reduced surface area.

Table 1

H₂O₂ concentration and the kinetic parameters of as-prepared catalysts.

Catalyst	H ₂ O ₂ concentration (mmol·L ⁻¹)	k_f (mmol·L ⁻¹ ·h ⁻¹)	k_d (h ⁻¹)
gCN	0.4	0.19	0.22
PLCN-15	1.0	0.32	0.26
PLCN-30	4.4	0.92	0.41
PLCN-45	3.0	0.64	0.29

Fig. 10. (a) The H₂O₂ production ability over as-prepared catalysts; (b) H₂O₂ production ability of PLCN-30 under different reaction conditions (b).

Fig. 10(b) shows the H_2O_2 production ability of PLCN-30 under different reaction conditions. AgNO_3 ($10 \text{ mmol}\cdot\text{L}^{-1}$) was added into the reaction system as an electron scavenger. Obviously, the H_2O_2 production ability of PLCN-30 is greatly suppressed by adding AgNO_3 . This indicates that the photogenerated electrons are responsible for the oxygen reduction to form H_2O_2 . The H_2O_2 is hardly detected in the absence of PLCN-30 or oxygen, confirming that H_2O_2 is formed by the photocatalytic O_2 reduction process. To confirm the hydrogen source in H_2O_2 , dimethylformamide (DMF, aprotic solvent) was added into the reaction system instead of water. No H_2O_2 was generated, confirming that H_2O is the hydrogen source of the reaction. The reaction results and structural properties of the catalyst, measured after PLCN-30 was reused five times, are listed in Table 2. The surface area and the concentration of N vacancies have not decreased, demonstrating stable photocatalytic performance.

We conclude that N vacancies, as active sites, play an important part in the H_2O_2 production ability of the catalyst. To confirm this hypothesis, we used Pd to cover the N vacancies on PLCN-30 by the photodeposition method [55]. Because of the considerable work function of platinum-group metals, Pd particles can be deposited on N vacancies selectively to prevent oxygen adsorption on specific N vacancies [56]. The obtained Pd-covered g- C_3N_4 is denoted as Pd-PLCN-30. Fig. 11(a) shows

Table 2

S_{BET} , C/N ratio, H_2O_2 concentration, and kinetic parameters of fresh and reused PLCN-30.

Catalyst	S_{BET} ($\text{m}^2\cdot\text{g}^{-1}$)	C/N ratio	H_2O_2 concentration ($\text{mmol}\cdot\text{L}^{-1}$)	k_{f} ($\text{mmol}\cdot\text{L}^{-1}\cdot\text{h}^{-1}$)	k_{d} (h^{-1})
Fresh	21.2	0.81	4.4	0.92	0.41
Reused	20.6	0.80	4.2	0.91	0.40

the PL spectra of gCN, PLCN-30, and Pd-PLCN-30 under O_2 atmosphere. The spectra show that the PL intensity of Pd-PLCN-30 is higher than that of PLCN-30, but still significantly lower than that of gCN because of the deposition of the precious metal. Interestingly, as shown in Fig. 11(b), Pd-PLCN-30 exhibits the same PL intensity under O_2 and Ar atmosphere. This indicates that the O_2 atmosphere cannot enhance electron transfer on Pd-PLCN-30, possibly because the N vacancies are covered by Pd particles, leading to poor oxygen adsorption ability. To confirm this premise, O_2 -TPD of Pd-PLCN-30 and PLCN-30 was conducted and the results are shown in Fig. 11(c). Obviously, compared with PLCN-30, the O_2 -TPD signal of Pd-PLCN-30 is almost negligible, confirming its poor oxygen adsorption ability. Fig. 11(d) shows the H_2O_2 production ability of Pd-PLCN-30 and PLCN-30. Unsurprisingly, Pd-PLCN-30 displays very low H_2O_2 production ability. All results confirm that N vacancies as active sites that considerably

Fig. 11. (a) PL spectra of as-prepared catalysts under O_2 atmospheres; (b) The comparison of PL intensity of Pd-PLCN-30 and PLCN-30 under Ar and O_2 atmospheres; (c) O_2 -TPD of Pd-PLCN-30 and PLCN-30; (d) The H_2O_2 production ability over Pd-PLCN-30 and PLCN-30.

affect the H_2O_2 production ability.

4. Conclusions

DBD plasma was used to synthesize a N-vacancy-doped g- C_3N_4 catalyst in situ under H_2 atmosphere for the first time. The results show that nitrogen vacancies are active centers, which can adsorb oxygen molecules and trap photoelectrons, thus promoting the transfer of photoelectrons from the catalyst to the adsorbed oxygen molecules for the subsequent reduction reaction. PLCN-30 exhibited the highest H_2O_2 concentration, 4.4 $\text{mmol}\cdot\text{L}^{-1}$, which is 11 times higher than that of gCN. Further extension of the plasma treatment time leads to a sharply decreased surface area, decreasing the number of active sites with exposure to the surface and thus leading to reduced photocatalytic performance.

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Graphical Abstract

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Preparation of N-vacancy-doped g- C_3N_4 with outstanding photocatalytic H_2O_2 production ability by dielectric barrier discharge plasma treatment

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N vacancies can chemisorb and activate O_2 molecules, thus promoting the transfer of photogenerated electrons from g- C_3N_4 to adsorbed O_2 molecules, leading to enhanced photocatalytic H_2O_2 production ability.

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介质阻挡放电等离子体法制备优异光催化合成过氧化氢性能的 氮空穴掺杂石墨相氮化碳

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摘要: 过氧化氢(H_2O_2)是一种绿色氧化剂, 广泛应用于纺织、印染、造纸和医药等行业。目前, 工业上采用蒽醌法制备 H_2O_2 , 它由于需要多步加氢和氧化处理, 因此能耗非常大。研究发现, 采用贵金属催化剂可以将氢气和氧气直接合成 H_2O_2 , 但催化剂价格过高, 且反应本身存在爆炸风险。近年来, 半导体光催化合成 H_2O_2 受到广泛关注。研究发现, 在水存在下, 光电子可以将氧气还原得到 H_2O_2 。介质阻挡放电(DBD)等离子体广泛应用于材料合成、挥发性有机物处理、汽车尾气净化和材料表面处理等。石墨相氮化碳($\text{g-C}_3\text{N}_4$)是新型非金属光催化剂, 以其性质稳定、能带适中和制备方便等优点而广受青睐。然而 $\text{g-C}_3\text{N}_4$ 的比表面积和电荷分离效率较低, 大大限制了其应用。

本文采用DBD等离子体法在氢气气氛下制备了N空穴掺杂的石墨相氮化碳, 采用XRD, N_2 吸附, UV-Vis, SEM, TEM, XPS, EIS, EPR, O_2 -TPD及PL等方法对催化剂进行了表征, 并考察了N空穴对催化剂结构性质、光学性质及光催化合成 H_2O_2 性能的影响。结果显示, 当DBD等离子体处理时间小于30 min时, 所制催化剂颗粒尺寸显著小于焙烧法得到的, 因而其比表面积显著提高。N空穴的引入降低了催化剂的能带, 提高了可见光区的吸收。此外, N空穴作为反应活性位, 既能吸附反应物氧气分子, 又能捕获光电子并促进光电子从催化剂向氧气分子转移, 进而发生后续还原反应。等离子体处理30 min得到的催化剂光催化合成 H_2O_2 性能最佳, 是纯 $\text{g-C}_3\text{N}_4$ 的11倍。本文为 $\text{g-C}_3\text{N}_4$ 基催化剂的制备提供了一个新方法。

关键词: 介质阻挡放电等离子体; 石墨相氮化碳; 过氧化氢合成; 氮空穴; 光催化

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